High-speed observation of the piston effect near the gas-liquid critical point

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We measured high-speed sound propagation in a near-critical fluid using a ultra-sensitive interferometer to investigate adiabatic changes of fluids on acoustic timescales. A sound emitted by very weak continuous heating caused a stepwise adiabatic change at its front with a density change of order 10^{-7}g/cm^3 and a temperature change of order 10^{-5}deg. Very small heat inputs at a heater produced short acoustic pulses with width of order 10μsec, which were broadened as they moved through the cell and encountered with the boundaries. The pulse broadening became enhanced near the critical point. We also examined theoretically how sounds are emitted from a heater and how applied heat is transformed into mechanical work. Our predictions well agree with our data.

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Thermal equilibration in one-component fluids takes place increasingly faster near the gas-liquid critical point at fixed volume [1, 2, 3, 4, 5, 6, 7, 8, 9, 10], despite the fact that the thermal diffusion constant D tends to zero at the criticality. This is because the thermal diffusion layer at the boundary expands and sounds emitted cause adiabatic compression and heating in the whole cell after many traversals in the container. This heating mechanism is much intensified near the critical point due to the critical enhancement of thermal expansion of the layer. If the boundary temperature T_w is fixed, the interior temperature approaches T_w on the timescale of the piston time [2],

$$t_1 = L^2/4(\gamma-1)^2 D, \tag{1}$$

where L is the cell length and $\gamma = C_p/C_V$ is the specific-heat ratio growing near the critical point. This time is much shorter than the isobaric equilibration time $L^2/4D$ by the very small factor $(\gamma-1)^{-2}$ [11].

The previous experiments have detected only slow temperature and density changes in the interior region on timescales of order 1 sec. The aim of this letter is to report ultra-sensitive, high-speed observation of sound propagation through a cell filled with CO_2 on the critical isochore close to the critical point $T_c = 304.12$K. We can detect density changes of order 10^{-8}g/cm^3 taking place on a timescale of 1μsec. In confined fluids, adiabatic changes are usually caused by a mechanical piston, but they can also be achieved by a heat input through a boundary [1, 2, 3, 4, 5, 6, 7]. The second thermoacoustic method is particularly efficient near the critical point. These adiabatic processes are very fundamental and ubiquitous, but we are not aware of any experiments detecting the underlying fast acoustic processes.

Our experimental set-up is displayed in Fig.1, where the fluid temperature was controlled with precision of

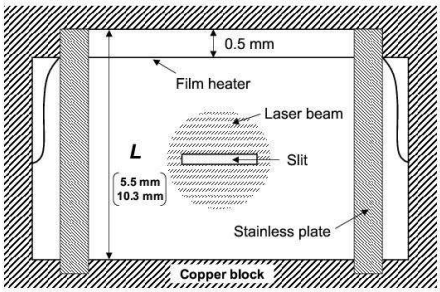

FIG. 1: Front view of experimental set-up. Cell length L is either 10.3mm or 5.5mm. A dc current is sent to a film heater placed 0.5mm below the top boundary. Light passing through the slit of width 0.25mm is used to detect small density changes using interferometry. Gravity is downward.

$\pm$1mK using a Pt-thermometer and a four-wire resistance bridge [12]. The upper and lower plates have area 1 cm^2 and are made of Cu with high thermal conductivity $\lambda_{\rm Cu}/k_B = 2.8\times10^{23}$/cm sec. The cell length L was either 10.3mm or 5.5mm. A thin NiCr-foil heater with thickness 3μm was placed $d = 0.5$mm below the top plate. The heat capacity of the foil is so small ($C_h/k_B = 8.4\times10^{19}$/cm^2 per unit area) and the generated heat was almost released to the fluid [13]. The side walls are made of stainless steel, whose thermal conductivity is 3.9% of that of Cu. We thus neglect heat flow to the side walls. A laser beam was sent at the cell center and a Twymann-Green interferometer was used to detect small density changes in a slit region of width 0.25mm. Individual signals were very noisy and the data

points in the following figures are the averages over 418 heat pulses successively generated in 2 seconds. Using sound pulses we first measured the sound speed c. For both $L = 10.3$mm and 5.5mm, our data on c closely agree with previous ones in the range $T/T_c - 1 \gtrsim 10^{-4}$ [14], but become independent of $T - T_c$ closer to the critical point because of the frequency-effect (inherent to short-time pulses) and/or the gravity effect [15].

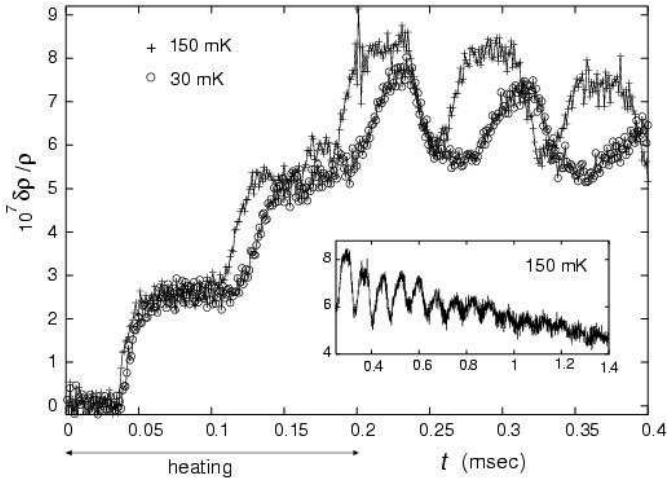

FIG. 2: Normalized density change $\delta\rho(t)/\rho$ at the cell center in the time region $0 < t < 0.4$msec for $T - T_c = 150$mK and 30mK, produced by continuous heating in $0 < t < 0.2$msec in a cell of $L = 1.03$cm. Inset: Long-time behavior for $T - T_c = 150$mK in the time region $0.2 < t < 1.4$msec.

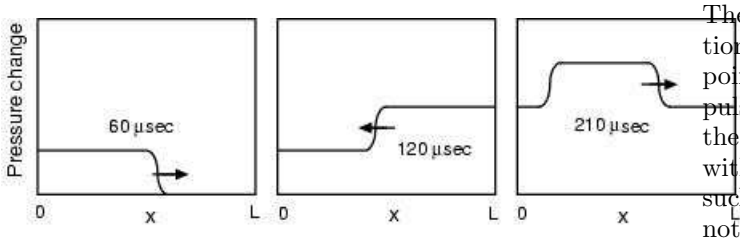

FIG. 3: Profiles of pressure deviations propagating at the sound speed at $T - T_c = 150$mK. Heating is stopped at $t = 200\mu$sec, which results in a trapezoidal pulse (right).

In Fig.2 we show acoustic density variations $\delta\rho(t)$ at the cell center $x = L/2$ in a cell of $L = 1.03$cm at $T - T_c = 150$ and 30mK, where $c \cong 140$ and 123m/sec, respectively. Continuous heating was applied in the time region $0 < t < 0.2$msec and a sound signal arrived at the cell center only for $t > (L/2 - d)/c \sim 40\mu$sec. The total heat supplied was $Q = 367$erg. The inset of Fig.2 displays a rapid relaxation at $T - T_c = 150$mK after switching-off the heater. Fig.3 illustrates spatial profiles of the pressure deviation δp, whose inhomogeneity remains small even in the thermal diffusion layers. Notice that $\delta\rho$ takes large negative values in the layers. The thickness of the layers was only 2.6×10^{-5}cm at $t = 0.2$msec for $T - T_c = 150$mK. Right after switching-on the heater, step-like sounds were emitted on both sides and the one moving upward was reflected at the top at $t \cong d/c$. The two pulses merged for $t > 2d/c \sim 10\mu$sec. After sweeping of the sound, we can see a stepwise increase in the density at $t \cong L/2c, 3L/2c$, and $5L/2c$. After the switching-off at $t = 0.2$msec, a trapezoidal pulse appeared moving back and forth in the cell. The trapezoidal part should be diminished if the heating time would be a multiple of $2L/c$. The interior temperature was slightly increased by $\delta T = (\partial T/\partial\rho)_s \delta\rho$ and a heat flow was induced through the boundaries. In the present case $\delta T \sim 0.2 T \delta\rho/\rho \sim 10^{-5}$deg. As can be seen in the inset of Fig.2, the subsequent relaxation in the interior region was very rapid. It is the same as that after cooling of the boundaries on long times scales ($t \gg L/a$), so it is an adiabatic process caused by contraction of the thermal diffusion layers.

In Fig.4 we show $\delta\rho(t)$ after very short heating in a cell of $L = 5.5$mm at $T - T_c = 500$ and 100mK, where $c \cong 149$ and 133m/sec, respectively. A dc electric current of duration time 4.5μsec passed through the heater, where the pulse shape was determined by the relaxation time 2μsec of the current amplifier. The total heat supplied was $Q = 129$erg. The pulse directly leaving downward and that reflected at the top can be distinguished since their peaks are separated by $2d/c$ (which is 6.7μsec for $T - T_c = 500$mK). Afterward, the two-peak pulse thus formed moved with speed c in the cell and was gradually flattened. In Fig.5 we show pulse propagation and its decay at $T - T_c = 500$ and 35mK in the cell of 1.03cm on a longer time scale, where the pulses are singly-peaked because of the longer pulse-duration time 7μsec ($> 2d/c$). The pulse broadening and the tendency of homogenization become more enhanced on approaching the critical point. In these experiments, the fluid velocity in the pulse region was of order $v = c\delta\rho/\rho \sim 10^{-2}$cm/sec and the fluid displacement was of order $\Delta x = v\Delta t \sim 10^{-7}$cm with $\Delta t \sim 10\mu$sec being the pulse-duration time. For such extremely small displacements the film heater did not disturb the sound propagation [16]. We are interested in the adiabatically increased energy $E_{\rm ad} (= p\Delta x)$ in the pulse region per unit area. To linear order it is expressed as

$$E_{\rm ad} = \frac{p}{\rho} \int dx \delta\rho(x,t) = \frac{pc}{\rho} \int dt \delta\rho(x,t). \qquad (2)$$

The ratio of $E_{\rm ad}$ to the total heat supplied $Q = \int dt \dot{Q}(t)$ represents the efficiency of transforming applied heat to mechanical work. In our experiments $E_{\rm ad}/Q$ was about $0.11 - 0.12$ at the first arrival of pulses at the cell center over wide ranges of $T - T_c$ and Q. However, a pulse has a tail persisting in later times and there remains ambiguity of order 10% in the calculation of $E_{\rm ad}$.

We give theoretical interpretations of the above results neglecting the effect of the bulk viscosity. Let a small amount of heat be supplied to a near-critical fluid at a rate $\dot{Q}(t)$ per unit area for $t > 0$ in a one-dimensional geometry. The volume expansion rate per unit area near

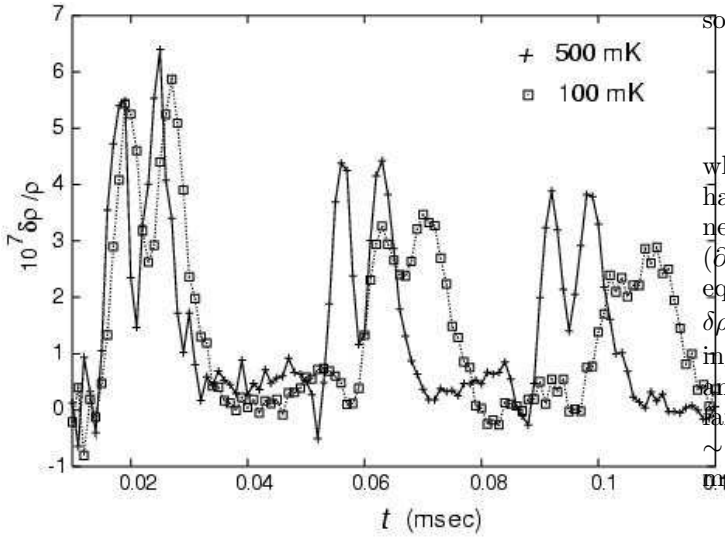

FIG. 4: $\delta\rho(t)/\rho$ at the cell center for $T - T_c = 500$mK and 100mK in the time region $0 < t < 0.12$msec, produced by pulse heating of width 4.5μsec in a cell of $L = 5.5$mm.

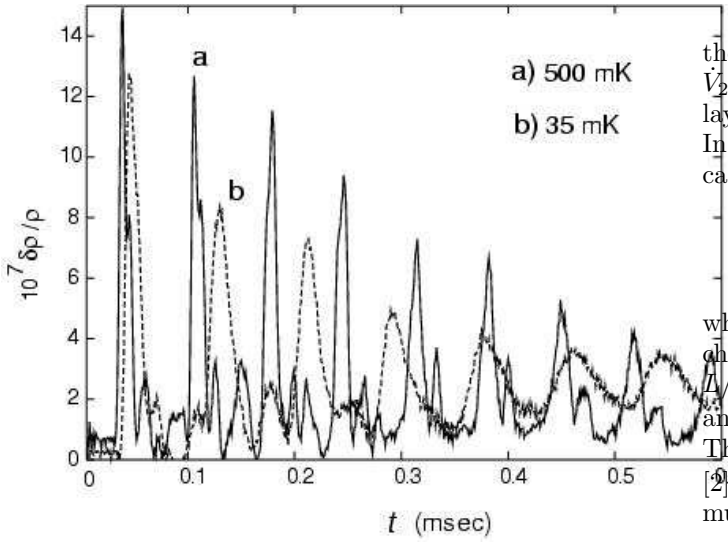

FIG. 5: $\delta\rho(t)/\rho$ at the cell center for $T - T_c = 500$mK and 35mK in the time region $0 < t < 0.6$msec, produced by pulse heating of width 7μsec in a cell of $L = 1.03$cm.

the heater is

$$\dot{V}_1 = \left(\frac{\partial\rho^{-1}}{\partial s}\right)_p \frac{\dot{Q}(t)}{T}, \tag{3}$$

where s is the entropy per unit mass. If the heater is attached to the upper plate, this volume change then produces a sound wave propagating downward as $\delta\rho_{\rm out}(t - x/c)$, where x is the distance from the heater and $\delta\rho_{\rm out}(t)$ is the density increase in the sound emitted at the heater at time t. Since acoustic disturbances move with the sound speed c, the mass conservation gives the sound amplitude,

$$\delta\rho_{\rm out}(t) = \frac{\rho}{c}\dot{V}_1 = \frac{\rho}{cT}\left(\frac{\partial T}{\partial p}\right)_s \dot{Q}(t), \tag{4}$$

where the Maxwell relation $(\partial\rho^{-1}/\partial s)_p = (\partial T/\partial p)_s$ has been used. The adiabatic coefficient $(\partial T/\partial p)_s$ is nearly equal to the derivative along the coexistence curve $(\partial T/\partial p)_{\rm cx}$ near the critical point [10]. For CO_2 it is equal to $T_c/6.98p_c$[15] and the above relation becomes $\delta\rho_{\rm out}/\rho = 1.38\times10^{-13}\dot{Q}$ with $\dot{Q}$ in erg/cm^{2}sec. The heating rate used for our data in Fig.2 was $\dot{Q} = 0.183\times10^7$ and then $\delta\rho_{\rm out}/\rho = 2.55\times10^{-7}$. This theoretical value fairly agrees with the observed height of the first step $\sim 2.2\times10^{-7}$ in Fig.2. The efficiency of energy transformation discussed below Eq.(2) becomes [2]

$$\frac{E_{\rm ad}}{Q} = \frac{p}{T}\left(\frac{\partial T}{\partial p}\right)_s, \tag{5}$$

which is $1/6.98 = 0.14$ for near-critical CO_2. On the other hand, the experimental values were in the range $0.11 - 0.12$.

As a complicating factor in our experiment, however, the heater is placed $d = 0.5$mm below the top plate. If $\dot{V}_2$ is the volume expansion rate in the thermal diffusion layer at the top plate, we require $c\delta\rho_{\rm out}(t)/\rho = \dot{V}_1 + \dot{V}_2$. In the time region where $(Dt)^{1/2} \ll d \ll ct < L$, some calculations yield a modified convolution-type formula,

$$\delta\rho_{\rm out}(t) = \frac{\rho}{cT}\left(\frac{\partial T}{\partial p}\right)_s \int_0^t dt'\dot{Q}(t-t')\dot{\psi}(t'/t_2)/t_2, \tag{6}$$

where $t_2 = L^2/4c^2t_1$ is a characteristic time of heat exchange between the boundary and sounds in the range $L/c \ll t_2 \ll t_1$. The scaling function $\dot{\psi}(u)$ is positive and its integral $\psi(u) = \int_0^u dv\dot{\psi}(v)$ tends to 1 for large u. The function $\psi(u)$ itself appeared in the original theory [2]. Thus Eq.(5) reduces to Eq.(3) when $\dot{Q}(t)$ changes much slower than t_2.

We clarify the relationship of the formula (3) and the assumption in the theory of the piston effect [2]. Let the heat input $\dot{Q}(t)$ changes slowly compared with the acoustic time $t_a = L/c$. We suppose a time interval with width $\delta t \gg t_a$, in which $\dot{Q}(t)$ is almost unchanged. After many sound traversals, the adiabatic pressure and density increases in the interior region are given by

$$\delta p = c^2\delta\rho = c^2\frac{\delta t}{t_a}\frac{\rho}{cT}\left(\frac{\partial T}{\partial p}\right)_s \dot{Q}, \tag{7}$$

as a result of superposition of many steps. In terms of the incremental heat supply $\delta Q = \dot{Q}\delta t$ we find

$$\delta p = \frac{\rho}{LT}\left(\frac{\partial T}{\partial \rho}\right)_s \delta Q = \left(\frac{\partial p}{\partial s}\right)_\rho \frac{\delta Q}{\rho TL}, \tag{8}$$

where the Maxwell relation $(\partial p/\partial s)_\rho = \rho^2(\partial T/\partial\rho)_s$ has been used. If δp is assumed to be homogeneous, Eq.(8)

follows from the space average of $\delta p = (\partial p/\partial s)_\rho \delta s + (\partial p/\partial \rho)_s \delta\rho$ [2], since the space integral of δs is $\delta Q/\rho T$ and that of $\delta\rho$ vanishes. In addition, the average temperature deviation is written as $\langle \delta T\rangle = \delta Q/C_V L$ where $C_V = \rho T(\partial s/\partial T)_\rho$ is the isochroic specific heat [10]. From Eq.(3) we may thus reproduce the original theory of the piston effect.

In summary, we have first measured rapid acoustic responses in near-critical CO_2 to extremely small heat inputs, which constitute a basis of understanding adiabatic processes in fluids. We demonstrate that adiabatic changes take place on the timescale of L/c. As Fig.2 suggests, it is intriguing that a homogeneous adiabatic change can be achieved almost instantaneously if the heating time is a multiple of $2L/c$. The theoretical expressions (3) and (4) are useful to analyze these results and can reproduce the original theory of the piston effect valid on long timescales. The theoretical height of a stepwise sound in Eq.(4) and efficiency $E_{\rm ad}/Q$ in Eq.(5) fairly agree with the experimental values. Differences of $20-30\%$ remain, probably because a fraction of heat escaped to the stainless part and the pulse shape was considerably broadened even at the first arrival at the cell center.

There are a number of unsolved problems. (i) We should understand how a sound pulse is reflected at a boundary wall and how it is damped in the bulk region. In our case, the change of the pulse shape on reflection is apparently more marked than that due to the bulk damping, as can be inferred from comparison of the results for $L = 5.5$mm and those for $L = 1.03$cm. This is still the case even very close to the critical point. (ii) The bulk viscosity exhibits strong critical anomaly as $\zeta \cong 0.03\rho c^2 t_\xi$ [10], where t_ξ is the order parameter relaxation time (18μsec at $T - T_c = 30$mK) [17]. It gives a bulk acoustic damping, but it also affects the thickness of the thermal diffusion layer when the typical timescale is longer than $\gamma\zeta/\rho c^2 \cong 0.03\gamma t_\xi$ [7, 8]. The effects of the bulk viscosity on heat transport are not yet well investigated, however. (iii) Upon heat exchange the wall temperature is not fixed when the effusivity ratio $a_w = (\lambda_w C_w/\lambda C_p)^{1/2}$ is small [3, 7]. Here λ_w, λ, C_w, and C_p are the thermal conductivities and the specific heats (per unit volume) of the solid and fluid, respectively. For finite a_w the piston time is given by $t_1{}' = [(1 + a_w^{-1})/(\gamma - 1)]^2 L^2/4D$ [3], which becomes $t_1' \cong C_V^2 L^2/4\lambda_w C_w$ for $a_w \ll 1$. In our case $a_w = 3\times 10^3 (T/T_c - 1)^{0.92}$ between Cu and CO_2 and $a_w < 1$ is reached for $T - T_c < 50$mK. This crossover should be studied.

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